# Modified Magnetism at a Buried Co/Pd Interface Resolved with X-Ray Standing Waves

Sang-Koog Kim* and J. B. Kortright

*Materials Sciences Division, Lawrence Berkeley National Laboratory, University of California, One Cyclotron Road, Berkeley, California 94720*

(Received 26 January 2000)

Soft x-ray standing waves produced by a multilayer interference substrate add depth sensitivity to magnetic circular dichroism to resolve changes in Co magnetism across a 1 nm distance from the Co center to the Co-on-Pd interface of a Pd/Co/Pd trilayer with an in-plane magnetization. Large enhancements of the number of Co $d$ holes, and of in-plane orbital and spin magnetic moments, are strongly localized at a thin, chemically modified interface layer. These results provide new insight into magnetic anisotropy at interfaces, and suggest a broad applicability of such standing wave measurements to interface magnetism studies.

DOI: 10.1103/PhysRevLett.86.1347 PACS numbers: 75.70.–i, 68.49.Uv, 73.20.–r

Interface magnetism is at the heart of much current magnetic research, driven by the discovery of new magnetic phenomena associated with interfaces and reduced dimension including giant magnetoresistance, magnetic tunneling junctions, exchange bias, and perpendicular magnetic anisotropy (PMA) [1]. As interface to volume ratios increase in magnetic nanostructures, the microscopic origin and details of these effects remain incompletely understood, because of both inherent microstructural complexity of nanometer thick layers and their interfaces and experimental difficulties resolving properties in depth in such structures.

Here we consider the reorientation transition from in-plane to PMA commonly observed for thin Co layers sandwiched between nonmagnetic metal layers as thickness decreases below 1 nm [2–10]. PMA is of renewed technological interest for high anisotropy films able to sustain sharp bit transitions in future high-density recording media. Néel's surface magnetocrystalline anisotropy (MCA) model [11] still underpins much fundamental understanding of PMA, in which a positive surface anisotropy term $K_S$ favors PMA because broken symmetry at the interface could result in an enhanced perpendicular orbital moment [9,12]. This surface term together with the negative volume anisotropy $K_V$ favoring in-plane anisotropy describe the total anisotropy $K = K_V + 2K_S/t$ for a film of thickness $t$. Reorientation occurs as $t$ decreases and $K$ changes sign, with $K_V$ and $K_S$ assumed independent of $t$ [6]. Experimental [6,9] and theoretical work [13] supports the notion of perpendicular surface MCA.

X-ray magnetic circular dichroism (MCD) studies of thin layers observe enhancements in orbital moments [14–18] and their perpendicular anisotropy [9,12] as $t$ decreases, from comparative measurements of ultrathin films of different or varying $t$. These MCD measurements typically average at least over 2–3 nm into the sample, and the interface moments are assumed not to change upon adding additional layers. Other work recognizes that local microstructural factors such as anisotropic strain [7,10] and possible chemical intermixing [10] are likely to be intertwined in the details of the reorientation by reducing the symmetry of the local crystal field, and that Co alloy films themselves can exhibit PMA [19]. Progress in discriminating between the simple surface MCA model and these complicating microstructural features has been slowed by the lack of experimental techniques that directly resolve changing magnetic properties in depth across buried interfaces of magnetic films only 1–2 nm thick.

In this Letter we address this limitation with an experimental technique explicitly able to distinguish magnetic properties at the magnetic/nonmagnetic interface from those just several atoms away at the center of the magnetic layer. We measure the Co $2p$ MCD spectrum while x-ray standing waves (SW's) selectively weight the absorption of different regions of the 2 nm Co film having overall in-plane anisotropy. Clear differences in Co spin-resolved and spin-averaged electronic structure are observed at the interfaces compared to the center of the film that have new implications for the PMA reorientation transition.

X-ray SW techniques are well established for obtaining depth-resolved structural information [20], and are used here to depth modulate the Co $L_{2,3}$ MCD spectrum as measured by total electron yield via sample drain current [21]. The magnetic system of interest, in this case a Pd/Co/Pd trilayer, is grown onto a multilayer interference structure that acts as a standing wave generator (SWG). As the incident x-ray beam is tuned across the SWG interference (Bragg) condition, a strong SW field is formed in the entire SWG/trilayer structure by the coherent superposition of incident and reflected waves. The SW phase can be varied by tuning scattering vector $q = 4\pi \sin\theta/\lambda$, where $\theta$ is the incident angle from grazing and $\lambda$ the wavelength. The SW field intensity $E^2(z, q)$ acts as a distorted wave that modulates the sample's absorption in depth.

The SWG/trilayer system was grown by magnetron sputtering onto an oxidized Si wafter with careful structural phasing to enable the SW antinode to be tuned from the Co-on-Pd interface into the center of the Co

  

layer. X-ray reflectivity characterization (Cu $K\alpha$) of the $[W/B_4C]_{40}$ SWG yields the SWG period of 3.89 nm and a static Debye-Waller roughness $\sigma = 0.3$ nm. The entire structure is then $[W(1.75\ nm)/B_4C(2.14\ nm)]_{40}/Pd(2.08\ nm)/Co(1.91\ nm)/Pd(1.04\ nm)$ with the Co layer structurally in phase with the SWG $B_4C$ layers. Values for Pd and Co thickness were consistently determined by Rutherford backscattering and x-ray fluorescence analyses. In this structure the SW antinode is near the Co-on-Pd interface at the center of the Bragg peak, and moves into the Co layer as $q$ decreases, as shown in Fig. 1. The ultrathin trilayer is a small optical perturbation to the SW field, and the difference in this perturbation with reversed magnetization for highly elliptical soft x rays is small even at the Co $L_{2,3}$ lines as determined by interference calculations using measured Co magneto-optical constants. X-ray magneto-optical Kerr effect hysteresis loops near the Co $L_3$ line confirm that the Co layer has in-plane easy axis, a coercive field $H_C = 160$ Oe, and more than 90% remanence when measured in plane up to 2 kOe. Goals in studying this relatively thick layer with overall in-plane magnetization are to resolve differences in magnetism at the interface from the layer center and relate these to the reorientation transition.

Absorption spectra were obtained using out-of-plane elliptical polarization with measured degree of circular polarization $P_C = 0.76$ in an applied field of $\pm 1$ kOe oriented along the incident beam. $\theta$ scans across the SW resonance at fixed $h\upsilon$ comprise the bulk of the data. $h\upsilon$ scans at fixed $\theta$ far from resonance aid in normalizing the data sets to the absorption surfaces in Fig. 2. Familiar Co $L_3$ and $L_2$ white lines are observed at 778 and 793 eV, respectively, and a strong SW resonance centered at $q = 0.17$ Å$^{-1}$ extends through each absorption surface. Away from the Co lines the SW resonance originates from the entire SWG/trilayer structure, and shows no helicity dependence. SW modulations at the Co lines are very different from those away from the lines, with distinct helicity dependence indicating that Co magnetism is not constant across the 2 nm Co thickness.

Interpolating data along lines of constant $q$ facilitates normalizing the helicity dependent absorption surfaces, since SW $E^2(z)$ is constant at fixed $q$ except for the small $h\upsilon$-dependent perturbation resulting from Co absorption. Interpolated spectra are normalized using a modification to standard techniques. First the preedge background is extrapolated and subtracted, and the result normalized to 1 in the postedge region. This removes the SW modulation away from the Co $L_{2,3}$ lines resulting from non-Co absorption, leaving Co absorption spectra normalized to a common per atom scale. This normalization is accurate in the limit that helicity dependent Co absorption features present no perturbation to the SW $E^2(z, q)$. Helicity-dependent calculated corrections deviating from 1 only across the $L_{2,3}$ lines are applied to the fixed-$q$ spectra to complete the normalization, and have little effect on results of MCD sum-rule analysis below.

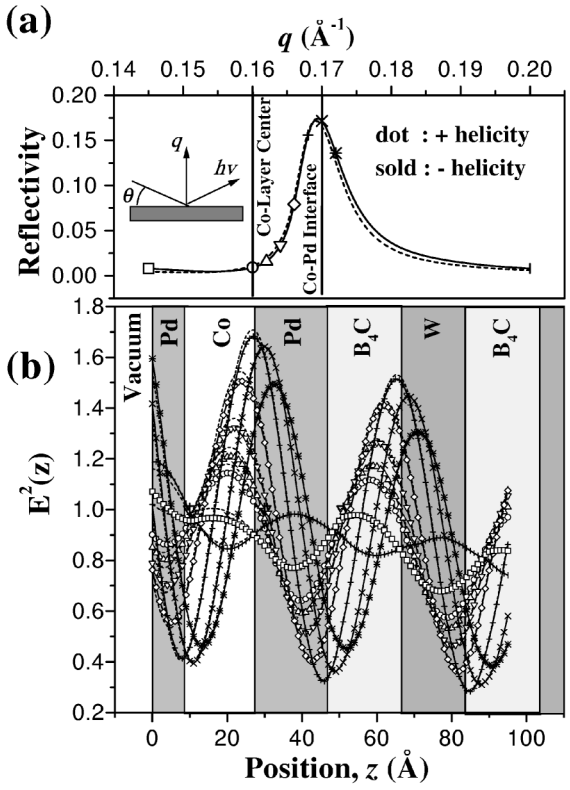


FIG. 1. Calculated reflectivities are shown at the Co $L_3$ line versus the scattering vector $q$ in (a). Interference of incident and reflected fields produce SW's versus depth, $z$ in the magnetic trilayer structure in (b). In each panel, solid and dotted lines refer to opposite helicities, and SW's are calculated at $q$ values indicated by the same symbols. The vertical lines in (a) indicate where the antinode of the SW is at the Co/Pd interface ($q = 0.17$ Å$^{-1}$) and in the center of the Co layer ($q = 0.16$ Å$^{-1}$).

Normalized results are summarized in Fig. 3 showing the helicity-averaged absorption in (a) and MCD surfaces in (b), corrected for $P_C$ and projected on the in-plane direction. Both data sets show clear structure at Co $L_{2,3}$ lines that result from changes in spin-resolved $d$-state occupation with position across the 2 nm Co layer. Depth resolution is obtained primarily from variations near the

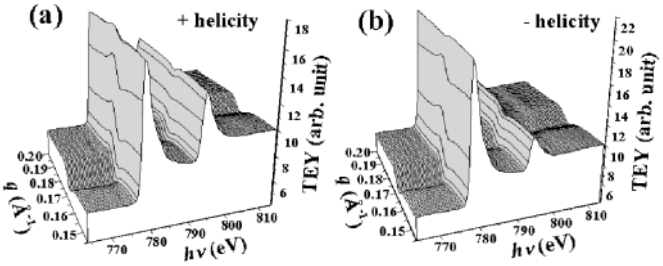


FIG. 2. Total electron yield (TEY) absorption spectra on a $(q, h\upsilon)$ surface, as measured with reversed magnetization, reveal SW modulations versus $q$.

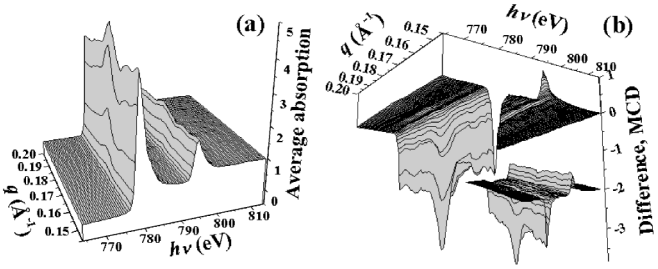


FIG. 3. Polarization-averaged absorption surface obtained from normalized helicity-dependent surfaces is in (a). MCD surface obtained from the difference of normalized spectra is in (b). The inset of (b) is another view of the same surface.

SW resonance ($0.16\ \text{Å}^{-1} < q < 0.18\ \text{Å}^{-1}$) as shown in Fig. 1. Thus, at the Bragg peak ($q \cong 0.17\ \text{Å}^{-1}$) Co absorption from atoms at the interface is weighted by a strong SW, and at $q = 0.16\ \text{Å}^{-1}$ Co absorption at the center of the Co layer is preferentially weighted by a much weaker SW. Comparing normalized absorption results at these two $q$ values thus reveals changes in Co absorption over just 1 nm, with some residual smearing due to the finite extent of the SW in depth. The number of $d$ holes, $n_h$, as well as orbital, $m_L$, and spin, $m_S$, magnetic moments are determined vs $q$ from the data in Fig. 3.

Variations of $n_h$ with depth are significant both because this quantity is essential in determining $m_L$ and $m_S$ and because they signal changing $d$-state occupancy across the layer. Strong variations in $n_h$ are clearly seen in the simultaneous increase in $L_3$ and $L_2$ intensity at $q = 0.17\ \text{Å}^{-1}$, and are quantified from changes in the total area of these lines assuming that the radial dipole matrix element remains constant across the Co layer [15,22]. The resulting variation of $n_h$ with $q$ is plotted in Fig. 4, with absolute value determined by scaling data outside the SW resonance to the value used in Ref. [23]. The peak in $n_h$ at $q = 0.17\ \text{Å}^{-1}$ reveals an excess in Co $d$ holes at the Co-on-Pd interface of at least 0.8 compared to the Co layer center. A modified Co electronic structure is localized at the interface, whose origin can be considered from the views of intermetallic bonding or band structure, whereby this increase implies charge transfer from Co to Pd at either a sharp or an intermixed interface, or a shift of the spin-averaged Co $d$ bands upward by hybridization with Pd resulting in a larger density above Fermi energy, respectively. In both views chemical modification by Pd is reasonably assumed to be involved with the changes in interfacial Co $n_h$.

Distinct interfacial enhancements are also resolved in $m_L$ and $m_S$ from sum rule [24] analysis utilizing determined $q$-dependent $n_h$ values. Because of a potentially considerable but unknown dipole contribution at the interface [22], an effective spin moment $m_{Se}$ and not the true $m_S$ is determined. $m_L$, $m_{Se}$, and their ratio are plotted vs $q$ in Fig. 4. $m_L$ is enhanced from $0.16\mu_B$ at $q = 0.16\ \text{Å}^{-1}$ to $0.5\mu_B$ at $q = 0.17\ \text{Å}^{-1}$, while $m_{Se}$ is enhanced by less than 20% at the interface. The peak in the $m_{Se}$ enhancement at slightly smaller $q$ than the $m_L$ peak suggests that a dipole component may exist at the interface. The ratio $m_L/m_{Se}$ is also enhanced at the interface.

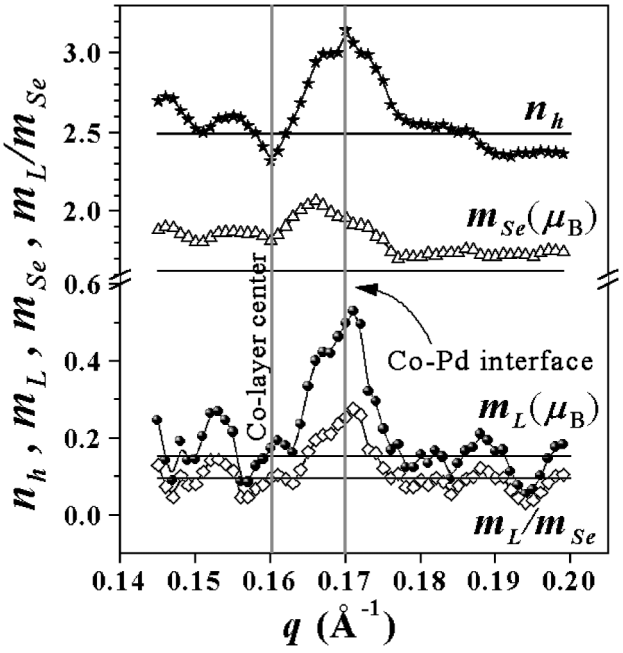


FIG. 4. Determined values of $n_h$, $m_{Se}$, $m_L$, and $m_L/m_{Se}$ vs $q$. All horizontal straight lines indicate values quoted from Chen *et al.* [23] for a 5–7 nm thick Co film.

Both the large size and the in-plane direction of the measured interfacial enhancement of $m_L$ are significant. The size must result at least in part from a redistribution of Co $3d$ electrons of interfacial atoms that is expected from the increase in $n_h$ and consistent with a changing average local environment of Co atoms at the interface. Since Pd has 3 times stronger spin-orbit coupling [25] than Co, hybridization of interfacial Co and Pd would also tend to increase interfacial Co $m_L$ by enhancing Co spin-orbit coupling. This is further evidence for chemical modification of interfacial Co by Pd nearest neighbors.

The in-plane direction of the observed enhancement of $m_L$ is evidence that the interfacial $m_L$ does not have perpendicular anisotropy as predicted by the simple surface MCA model. Only in-plane values of $m_L$ can be measured with this SW technique because it is impossible to generate a SW using resonant radiation perpendicular to the interfaces. Thus, while anisotropy of the $m_L$ enhancement at the interface is not directly measured here, the measured large in-plane result does not support perpendicular anisotropy of this quantity. Rather, measured in-plane hysteresis loops show almost complete saturation above $H_C$, with no indication of a moment greater than $0.5\mu_B$ having perpendicular anisotropy that should be apparent as a small sheared hard-axis component. Furthermore, the size of the interfacial $m_L$ observed here is larger than perpendicular $m_L$ values reported for even thinner Co layers exhibiting complete PMA [8,14], making an even larger perpendicular component unlikely for this sample.

The transition to PMA must involve both the chemically modified interface layers and the more bulklike Co at the center of the layers. If PMA results solely or predominantly from surface MCA via broken symmetry, then it must be present at all interfaces and only then would $K_S$ be independent of $t$. However, this work presents evidence that in-plane, not perpendicular, anisotropy in $m_L$ exists at the interface of this relatively thick film. Since the anisotropy properties of this interface layer must determine $K_S$, this work thus suggests that $K_S$ is not independent of $t$, and that the two term anisotropy model ($K = K_V + 2K_S/t$) is oversimplified at the microscopic level. Nonetheless, the modified Co magnetism in these interface layers must be a precursor to PMA [19]. The apparent in-plane anisotropy of the interfacial $m_L$ could result from several microstructural or coupling effects, including anisotropy in spin-orbital coupling [26], exchange coupling [27], and crystal field modification. As $t$ decreases the bulklike Co is consumed by the more alloylike transition layers, whose anisotropic intermixing and strain properties may also depend on $t$ [7,10]. In this model the reorientation from in-plane to PMA may occur when all bulklike Co is consumed by the interface layers, yielding an ultrathin alloylike layer with very different properties than the interfaces of the thicker layer [28]. Previous results [7,19,27–30] that anisotropic strains are more sensitive to $t$ than is broken symmetry and that chemical mixing commonly occurs at typical heterointerfaces could support this model for reorientation transitions versus $t$.

In conclusion, the standing wave technique in conjunction with MCD has provided the first direct depth-resolved information on changing electronic and magnetic properties across a buried layer by identifying a chemically modified interface layer. Even with new insight gained in this depth-resolved study, further questions remain to be answered regarding the details of the reorientation transition. The results also clearly point out that it is dangerous to attempt to obtain bulk values for resonant x-ray magneto-optical constants using ultrathin films because of these interface layers. Extensions of the SW technique used here should provide new opportunities to depth-resolve electronic and magnetic structure in other magnetic interface systems.

We appreciate useful discussion with C. Fadley, G. van der Laan, S. Bader, J. Stöhr, and E. Fulleton. S.-K. K is indebted to V. A. Chernov for stimulating discussion. Measurements were made at ALS beam line 9.3.2 at LBNL. This work is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. DOE under Contract No. DE-AC03-76SF00098.

*Current address: Department of Physics and Center for Nanospinics of Spintronic Materials, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea. Electronic address: sangkoog@kaist.ac.kr

[1] See, e.g., J. B. Kortright *et al.,* J. Magn. Magn. Mater. **207**, 7 (1999).
[2] P. F. Carcia, A. D. Meinhaldt, and A. Suna, Appl. Phys. Lett. **47**, 178 (1985).
[3] B. N. Engel *et al.,* Phys. Rev. Lett. **67**, 1910 (1991).
[4] M. T. Johnson *et al.,* Phys. Rev. Lett. **69**, 3575 (1992).
[5] F. J. A. den Broeder *et al.,* J. Magn. Magn. Mater. **93**, 562 (1991).
[6] M. T. Johnson *et al.,* Rep. Prog. Phys. **59**, 1409 (1996).
[7] C. H. Lee *et al.,* Phys. Rev. B **42**, 1066 (1990).
[8] D. Weller *et al.,* Phys. Rev. B **49**, 12 888 (1994).
[9] D. Weller *et al.,* Phys. Rev. Lett. **75**, 3752 (1995).
[10] S.-K. Kim *et al.,* J. Magn. Magn. Mater. **170**, L7 (1997).
[11] L. Néel, J. Phys. Radium **15**, 376 (1954).
[12] J. Stöhr and H. König, Phys. Rev. Lett. **75**, 3748 (1995).
[13] J. G. Gay and R. Richter, Phys. Rev. Lett. **56**, 2728 (1986); G. H. Daalderop *et al., ibid.* **68**, 682 (1992); P. Bruno, Phys. Rev. B **39**, 865 (1989); O. Eriksson *et al., ibid.* **41**, 11 807 (1990); A. J. Freeman and R. Wu, J. Magn. Magn. Mater. **100**, 497 (1991).
[14] Y. Wu *et al.,* Phys. Rev. Lett. **69**, 2307 (1992).
[15] M. G. Samant *et al.,* Phys. Rev. Lett. **72**, 1112 (1994).
[16] M. Tischer *et al.,* Phys. Rev. Lett. **75**, 1602 (1995).
[17] N. Nakajima *et al.,* Phys. Rev. Lett. **81**, 5229 (1998).
[18] H. A. Dürr *et al.,* Phys. Rev. B **58**, R11 853 (1998).
[19] S.-K. Kim *et al.,* Appl. Phys. Lett. **71**, 66 (1997).
[20] M. J. Bedzyk *et al.,* Science **248**, 52 (1990); Y. L. Qian *et al., ibid.* **265**, 1555 (1994); A. Kazimirov *et al., ibid.* **282**, 930 (1998).
[21] Because the Co layer is so thin, possible saturation effects in TEY measurement are negligible, as demonstrated in Fig. 1 that shows a large penetration depth compared to electron escape depths. See R. Nakajima, J. Stöhr, and Y. U. Idzerda, Phys. Rev. B **59**, 6421 (1999).
[22] J. Stöhr, J. Electron Spectrosc. Relat. Phenom. **75**, 253 (1995).
[23] C. T. Chen *et al.,* Phys. Rev. Lett. **75**, 152 (1995).
[24] B. T. Thole *et al.,* Phys. Rev. Lett. **68**, 1943 (1992); P. Carra *et al., ibid.* **70**, 694 (1993).
[25] A. S. Chakravarty, *Introduction to the Magnetic Properties of Solids* (John Wiley and Sons, New York, 1980), p. 66.
[26] G. van der Laan, Phys. Rev. Lett. **82**, 640 (1999).
[27] H. A. Dürr *et al.,* Science **277**, 213 (1997).
[28] S.-K. Kim *et al.,* Phys. Rev. B **53**, 11 114 (1996).
[29] J. Lee *et al.,* Phys. Rev. B **55**, 15 103 (1997).
[30] K. Kyuno, J.-G. Ha, R. Yamamoto, and S. Asans, Phys. Rev. B **54**, 1092 (1996).